



# **Role of Microstructure on the Performance of UHTCs**

Sylvia M. Johnson, Matt Gasch, John Lawson  
NASA Ames Research Center

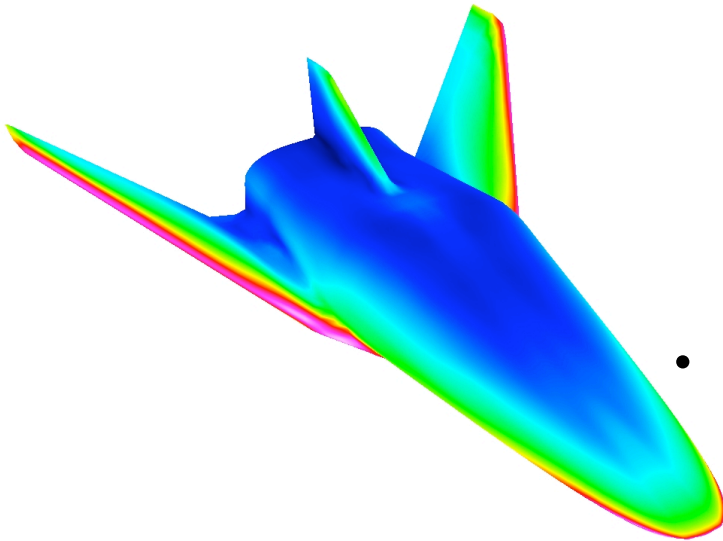
Mike Gusman, Mairead Stackpoole  
ELORET Corporation

34th International Conference and Exposition on Advanced  
Ceramics and Composites  
Daytona Beach, FL January, 2010



# Sharp Leading Edge Technology

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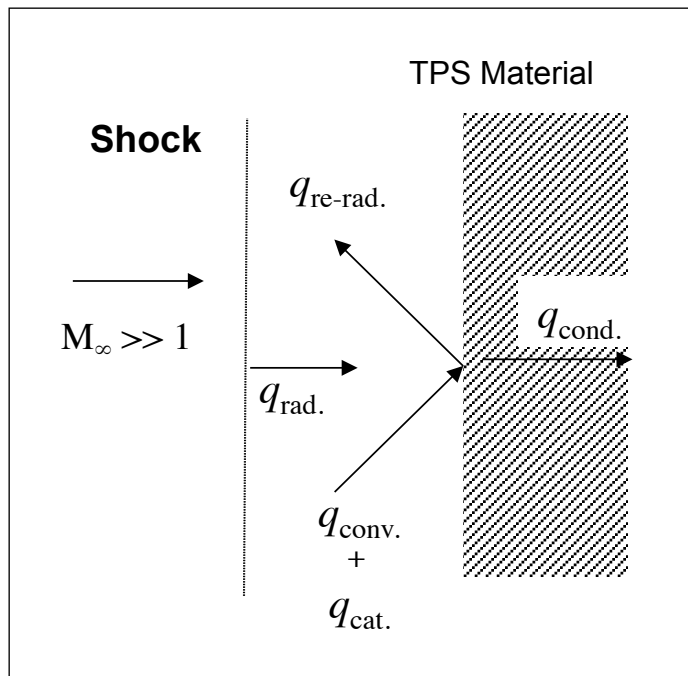


- Sharp leading edge technology
  - Enhances vehicle performance
  - Leads to improvements in safety
    - Increased vehicle cross range
    - Greater launch window with safe abort to ground
- Sharp leading edges place significantly higher temperature requirements on the materials:
  - Current shuttle RCC leading edge materials:  $T \sim 1650\text{ }^{\circ}\text{C}$
  - Sharp leading edged vehicles will require:  $T > 2000\text{ }^{\circ}\text{C}$

*Ultra High Temperature Ceramics are candidates for use in sharp leading edge applications.*



# UHTC Material Property Considerations



$$q_{\text{re-rad.}} = \varepsilon_w \sigma T_w^4, \text{ where } \varepsilon_w = \text{emissivity}$$

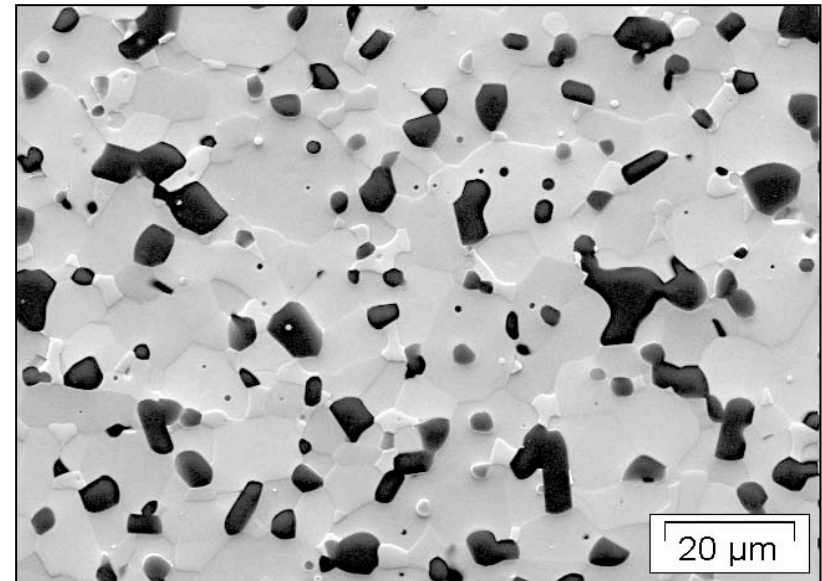
- Emittance determines amount of re-radiated energy.
  - **Emittance should be as high as possible**
  - Surface oxidation can reduce emittance
- Thermal diffusivity determines amount of energy conducted within the material.
- High thermal conductivity is desirable in sharp leading edge applications.
  - Enhances vehicle performance
  - Increases thermal shock resistance
- Catalycity determines amount of chemical energy released near the surface due to recombination of dissociated species.
  - Surface catalycity should be low
  - Catalycity estimated from temperature measurements during arcjet experiment
  - If facility conditions are known and material properties (such as emittance and thermal diffusivity) are known, then the heating from catalycity can be estimated.



# Outline

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- Experimental approach
- Results
  - Strength/fracture toughness
  - Thermal conductivity
  - Oxidation resistance
- Computational approach



HfB<sub>2</sub>/20v%SiC  
Hot Pressed (Baseline)



# UHTC Research at NASA Ames

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- Controlling microstructure and composition to improve properties
  - Strength
  - Fracture toughness
  - Thermal conductivity
  - Oxidation resistance in re-entry
- Focus has been on monolithic materials and in situ composites
- Goal is to incorporate our research into both monolithic and composite materials



# UHTC Suitability for TPS

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- UHTCs are only for specialized TPS applications for which other material systems are not as capable or straightforward or their capabilities are required when active cooling is not feasible.
- Choice of materials driven by design, environment, and material properties.
  - Feasible simple nose-cone and passive-leading-edge designs have been developed. (UHTC leading edge designs use small volumes of material.)
  - UHTCs have high temperature capabilities ( $> 2000\text{ }^{\circ}\text{C}$  /  $3600\text{ }^{\circ}\text{F}$ )
- Material selection should be based on appropriate testing of matured material in relevant environment.
- Concerns about monolithic UHTC properties are being addressed by processing and engineering improvements (ceramic matrix composites [CMCs])



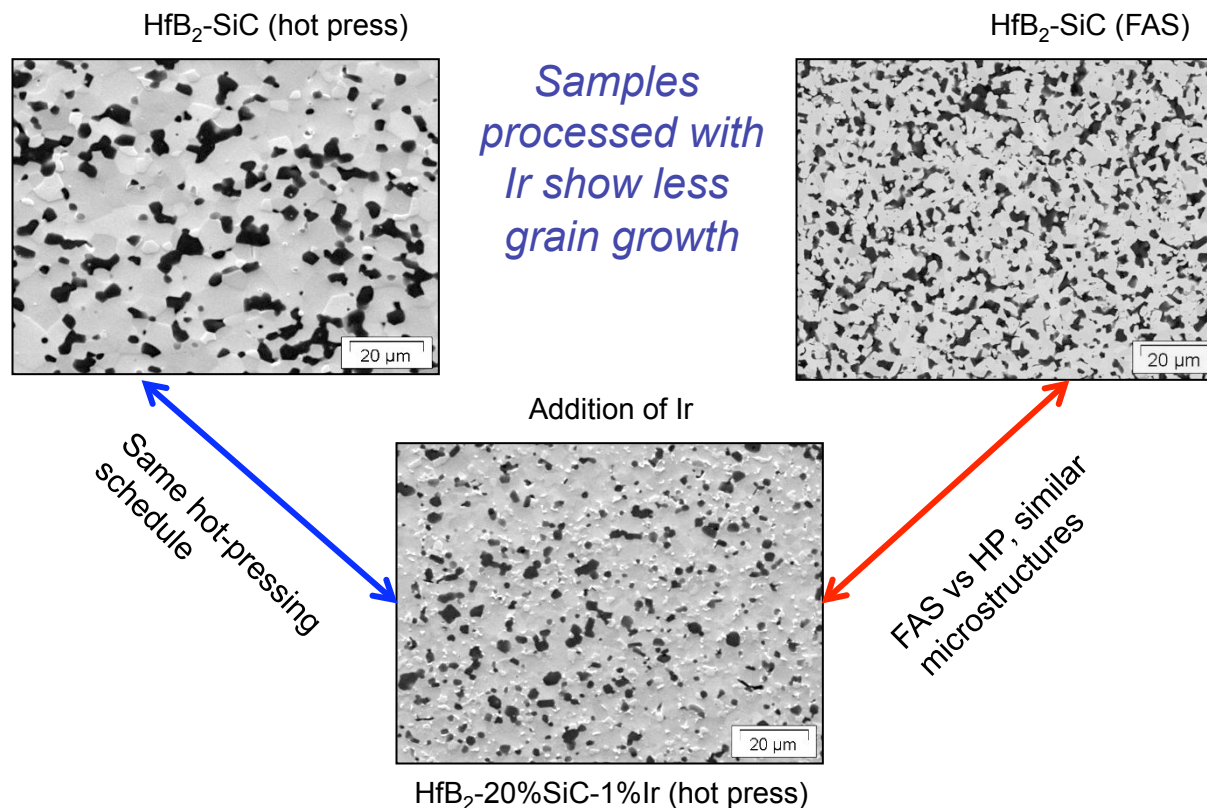
# Controlling Microstructure & Composition

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- Control grain size
  - Additives (Ir additions)
  - Processing by field-assisted sintering (FAS)
- Control grain shape
  - Addition of preceramic polymers
  - Particle coatings (Fluidized Bed CVD)
- Control purity (grain boundaries)
  - Addition of preceramic polymers
  - Processing (FB CVD)
  - Self-propagating reactions
- Control oxide formation
  - Increase oxide stability / emissivity (additives)
  - Reduce amount of SiC



# Controlling Grain Size



- Additives (Ir additions) — improve microstructures of hot-pressed materials to match that of FAS materials (very refined)
- Processing (FAS) — refined microstructure

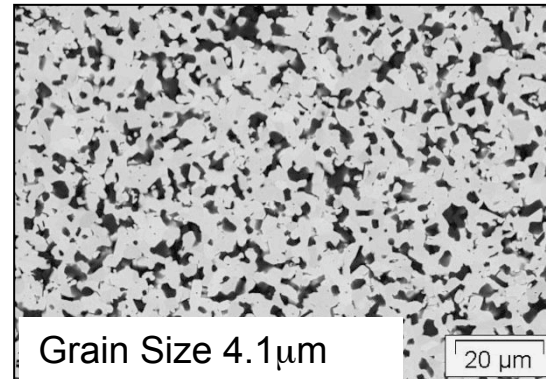
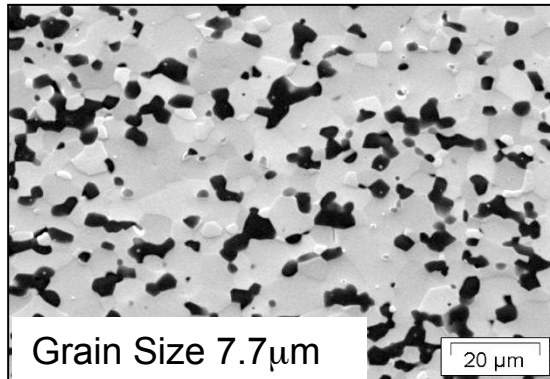




# Physical Characterization: Microstructure

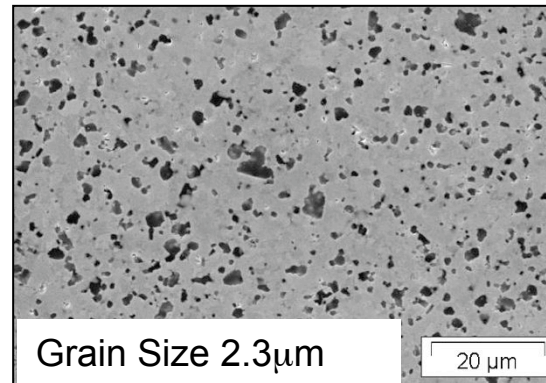
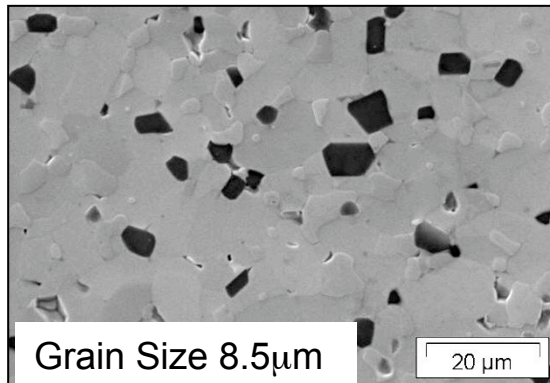
Hot Pressed

HfB<sub>2</sub>-SiC  
Baseline

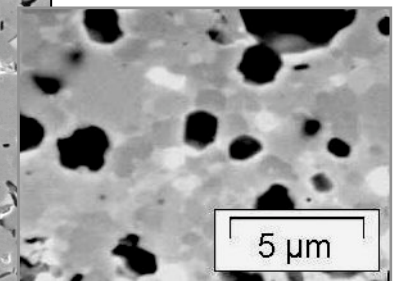
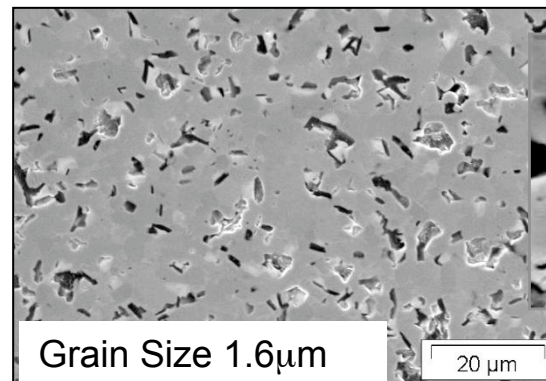
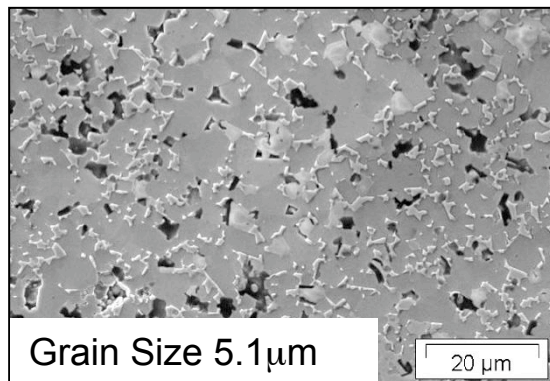


Field-Assist  
Sintered (FAS)

HfB<sub>2</sub>-SiC-TaSi<sub>2</sub>

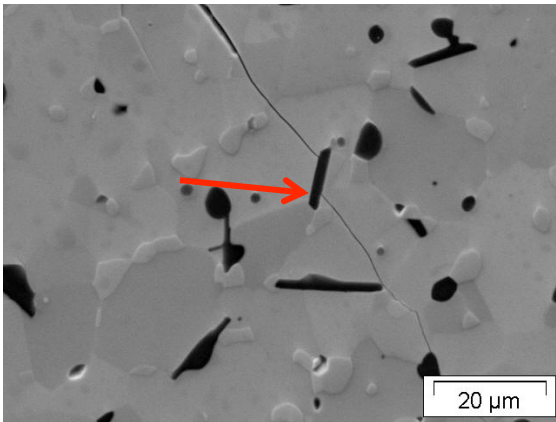
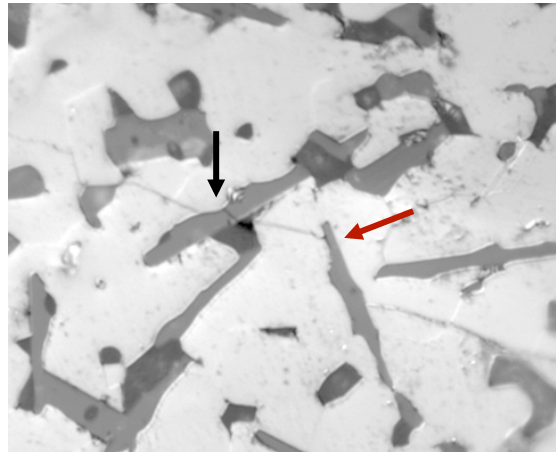
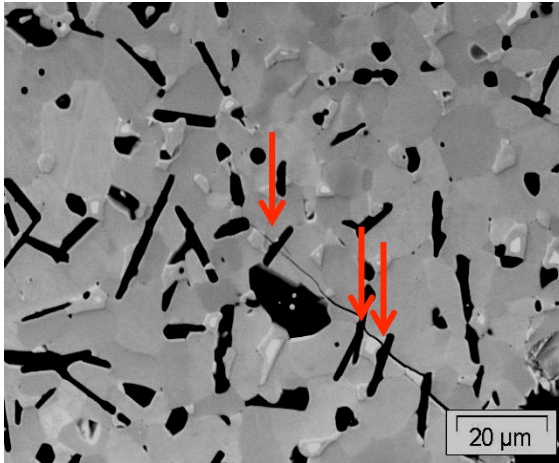


HfB<sub>2</sub>-SiC-  
TaSi<sub>2</sub>-Ir

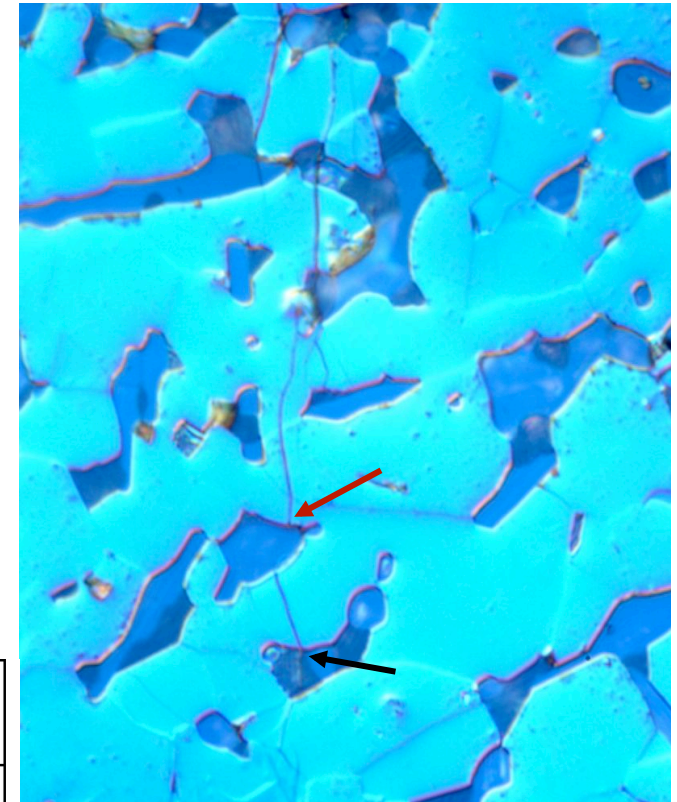




# In Situ Composite for Improved Fracture Toughness



SiC Content	Fracture Toughness (MPam <sup>1/2</sup> )
5%	3.61
10%	4.06
15%	4.47
Baseline UHTC (20%)	4.33



Oak Ridge National Laboratory

Evidence of crack growth along HfB<sub>2</sub>-SiC interface, with possible SiC grain bridging



# What About Active Oxidation?

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- Silicon-containing materials will actively oxidize under high temperature, low pressure conditions, forming SiO as gas
- Most problematic during re-entry (not during cruise)
- Mitigation approaches:
  - Reduce volume of SiC
    - Reduce overall oxidation
    - Below percolation threshold
  - Reduce scale of SiC particles
    - Allows formation of protective oxide sooner
    - Increase tortuosity of diffusion path
    - Balance between control of grain size and limit of oxidation
  - Additives
    - To change viscosity of the oxide
      - Change emissivity (lower surface temperature)
      - Change diffusivity of species through the oxide
    - To form a physical barrier
    - To change sintering behavior of UHTC with consequent reduction in SiC



# Controlling the Composition of Oxides

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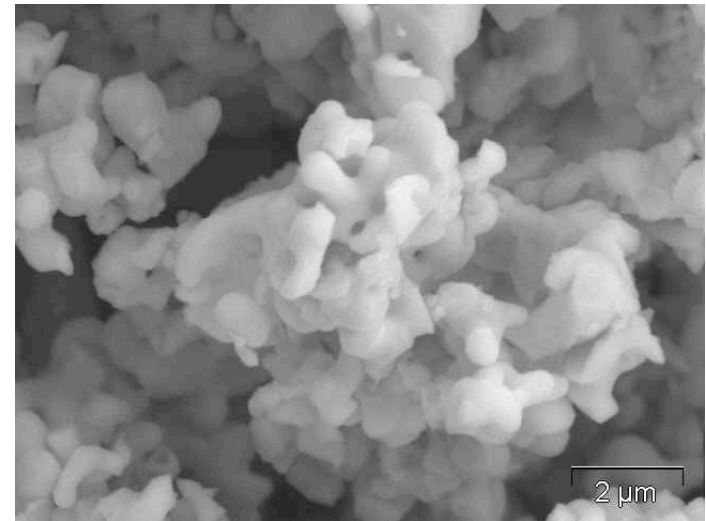
- High temperature use of UHTCs will form surface oxides
  - Composition of resultant surface oxide is an important factor when considering:
    - Protective characteristics of newly formed surface may be dependent on its viscosity and CTE
    - Emissivity characteristics of oxides
    - Temperature capability (mp) of the oxide
    - oxidation resistance
- Investigating the effects of additives to address these goals
- Using FBR-CVD and reactive pressing to add:
  - Rare earths
  - Transition metals



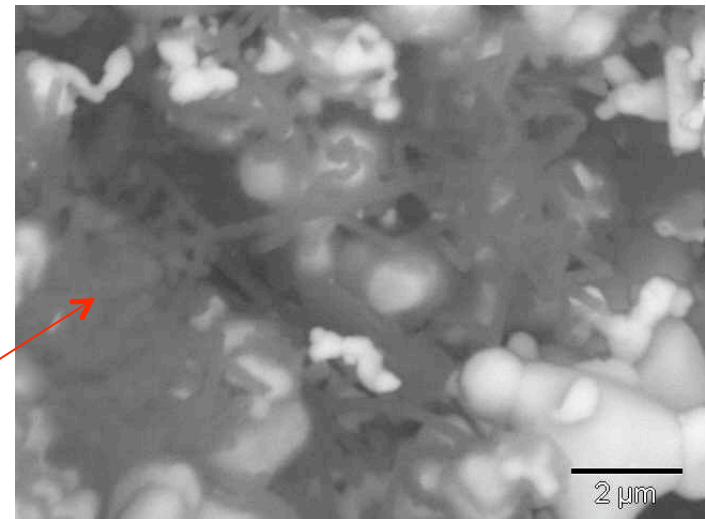


# Additives as CVD Coatings and Reactive Powders

- Using CVD coatings applied in a Fluidized Bed Reactor, instead of particles, it is possible to:
  - Distribute a uniform and controlled coating
  - Bypass traditional sources of processing contamination
  - Improve oxidation and creep resistance (less  $O_2$  contamination)
  - Control amount of additive
- Standard composition starts with “as received”  $HfB_2$ 
  - powder coated with B, Si, & C, after pretreatment with  $H_2$
  - Forms filamentous SiC (amorphous)



As received  $HfB_2$



Coated  $HfB_2$



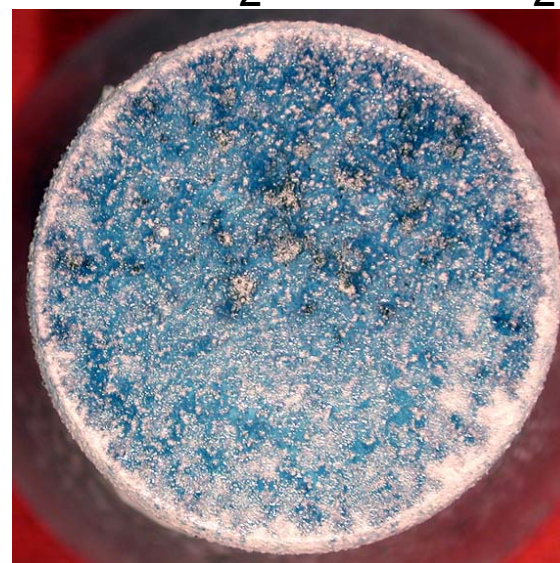
# Increasing Oxide Emissivity

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HfB<sub>2</sub>-SiC



HfB<sub>2</sub>-SiC-TaSi<sub>2</sub>


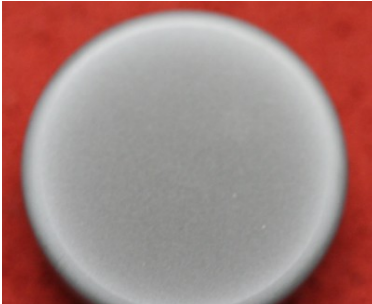
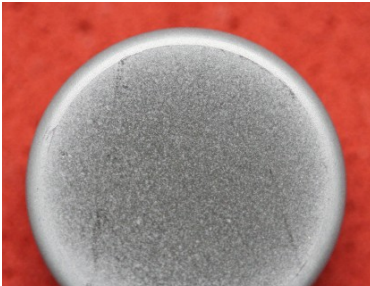
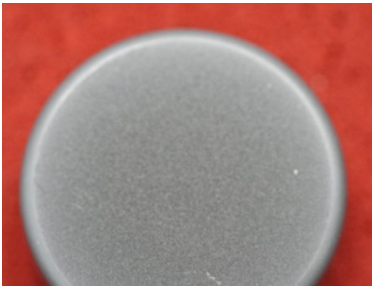




- Arcjet test: Performance of HfB<sub>2</sub>/SiC-TaSi<sub>2</sub> **comparable** to HfB<sub>2</sub>/SiC after testing for 5 minutes at  $Q_{cw} \sim 300 \text{ W/cm}^2$
- HfB<sub>2</sub>/SiC-TaSi<sub>2</sub> clearly has a higher post-test emissivity than HfB<sub>2</sub>/SiC and demonstrated lower surface temperatures

Opila, E. and Levine, S., "Oxidation of ZrB<sub>2</sub>- and HfB<sub>2</sub>-based ultra-high temperature ceramics: Effect of Ta additions," *Journal of Materials Science* 39 (2004) 5969–5977



# Arcjet Characterization: Surface

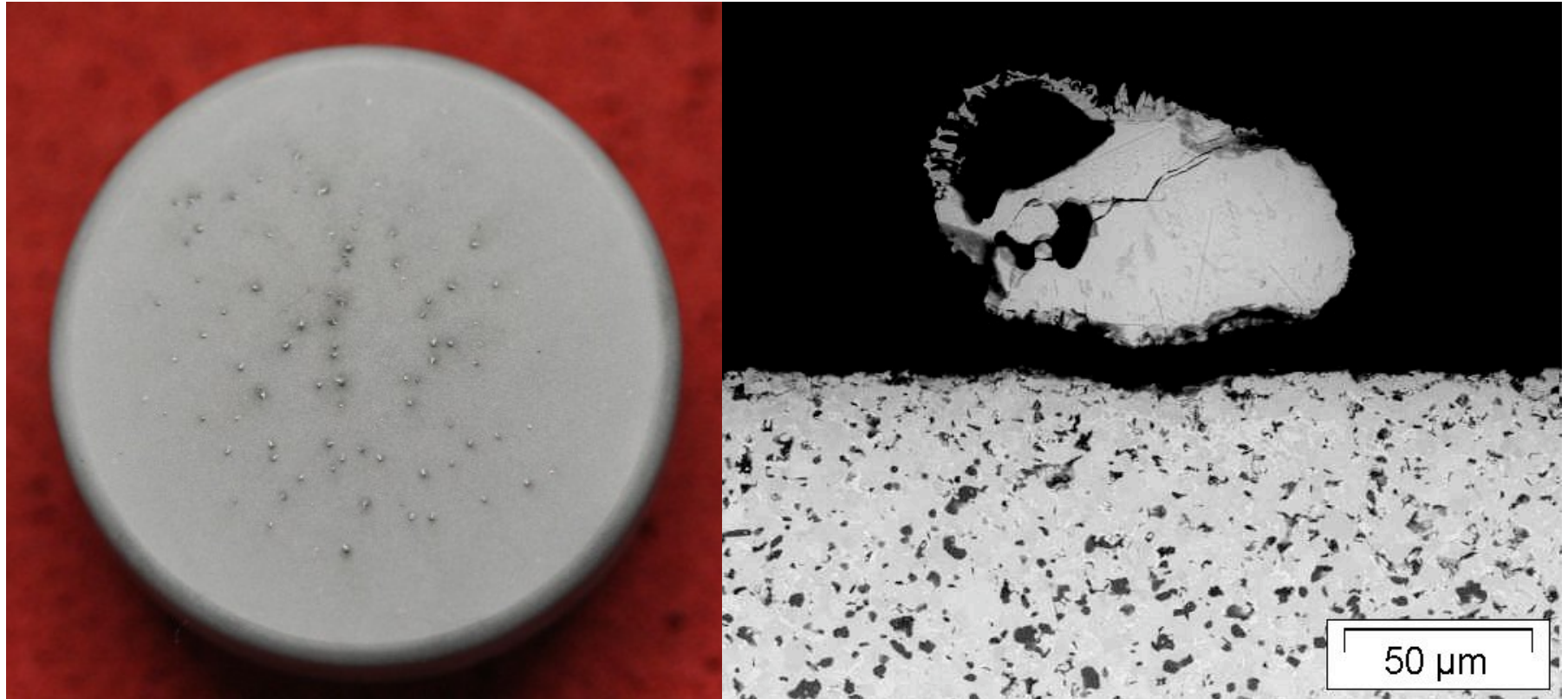
	Hot Pressed	Field Assist Sintered
HfB <sub>2</sub> -SiC Baseline	 Emittance = 0.65	 Emittance = 0.87
HfB <sub>2</sub> -SiC-TaSi <sub>2</sub>	 Emittance = 0.89	 Emittance = 0.89
HfB <sub>2</sub> -SiC-TaSi <sub>2</sub> -Ir	 Emittance = 0.87	 Did not arcjet test. Sample cracked during fabrication





# Arcjet Characterization

$\text{HfB}_2\text{-SiC-TaSi}_2\text{-Ir}$



Close up of arcjet model with iridium, showing surface accumulation of Ir and corresponding SEM cross section



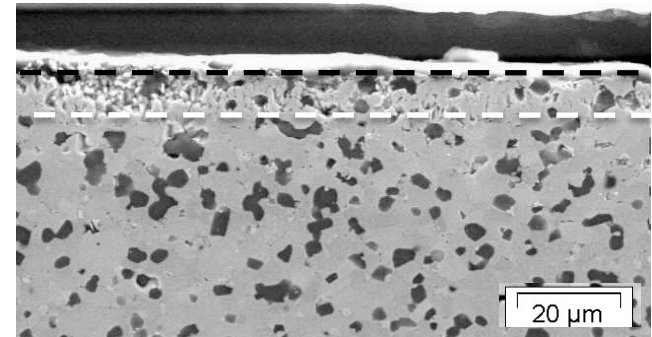
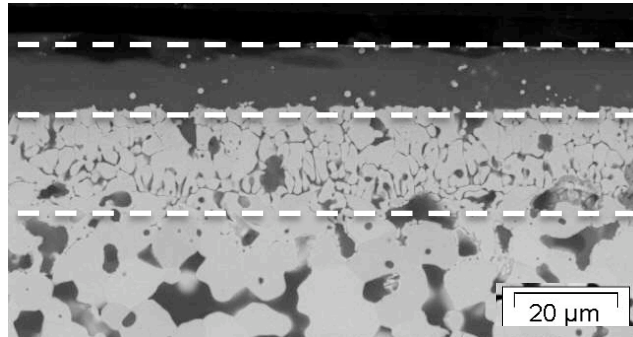


# Arcjet Characterization: Additives & Influence of Microstructure

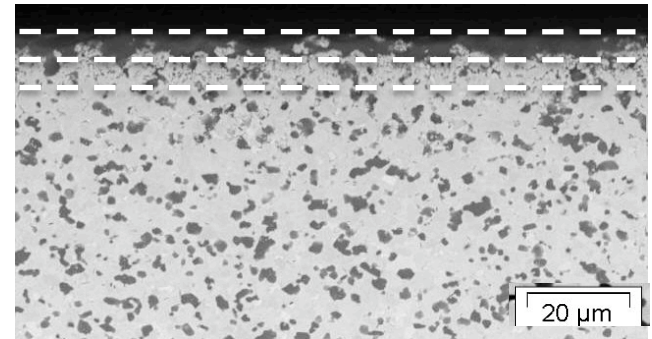
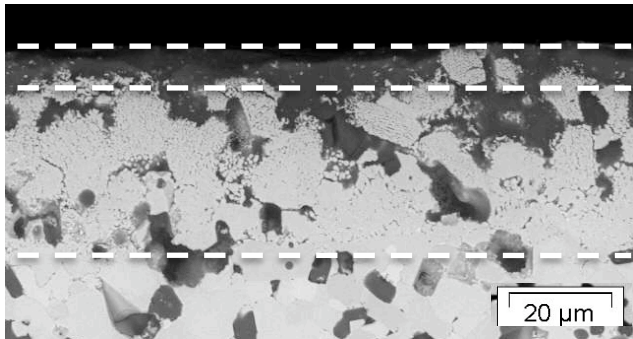
**Hot Pressed**

**Field Assist Sintered (FAS)**

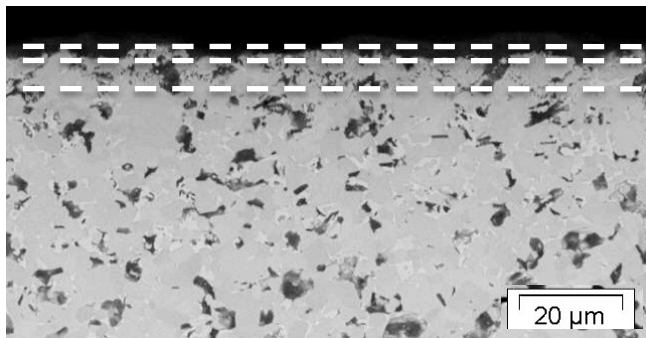
HfB<sub>2</sub>-SiC  
Baseline



HfB<sub>2</sub>-SiC-TaSi<sub>2</sub>



HfB<sub>2</sub>-SiC-  
TaSi<sub>2</sub>-Ir



Both oxide scale  
and depletion zone  
can be reduced.



# Arcjet Characterization: Summary

- Additions of  $\text{TaSi}_2$  seem to improve oxidation resistance of coupons fabricated with either HP or FAS. However, the sample fabricated by HP has a large SiC depletion zone, similar to the baseline material.
- Samples processed with iridium showed improved oxidation resistance and much smaller SiC depletion zones, in comparison to the baseline.

Model ID	Sinter Method	Heat Flux (W/cm <sup>2</sup> )	Pstag (atm)	Duration (sec)	Oxide Layer (μm)	SiC Depletion (μm)
HfB <sub>2</sub> -SiC (Baseline)	Hot Press	300	0.19	600	13	24
HfB <sub>2</sub> -SiC	FAS	250	0.10	600	3	8
HfB <sub>2</sub> -SiC-TaSi <sub>2</sub>	Hot Press	250	0.10	600	7	34
HfB <sub>2</sub> -SiC-TaSi <sub>2</sub>	FAS	250	0.10	600	3	6
HfB <sub>2</sub> -SiC-TaSi <sub>2</sub> -Ir	Hot Press	250	0.10	600	4	9



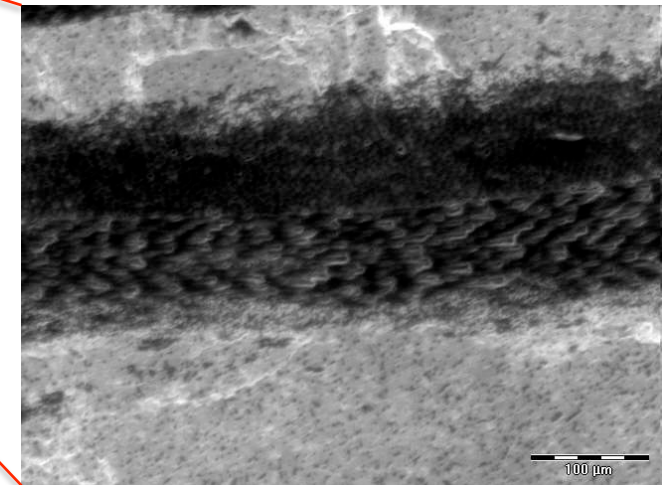
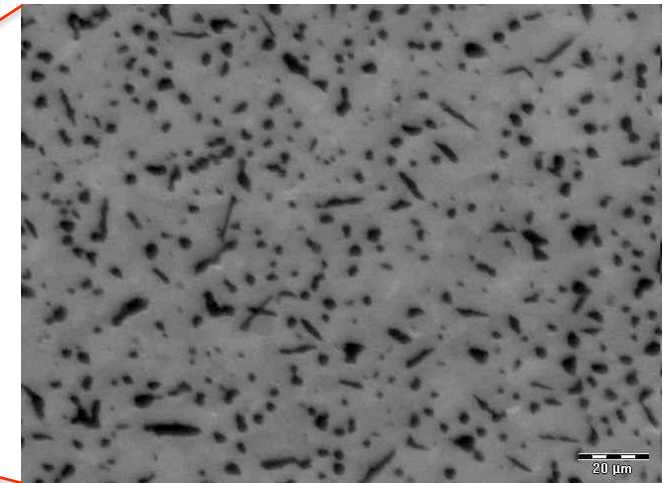
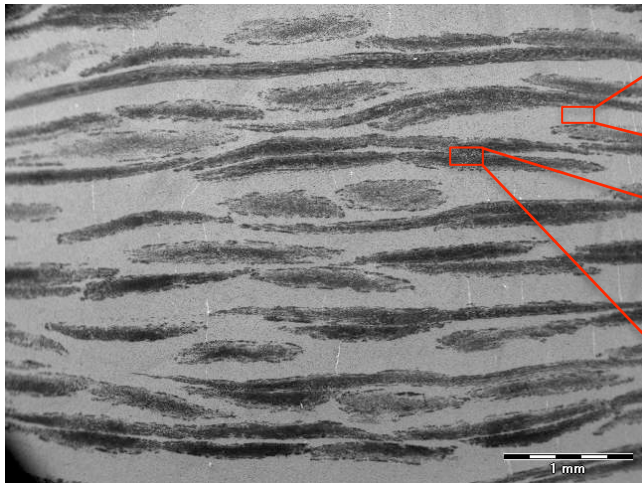
## Some Recent Work

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- Experimental effort
  - Initially focused on optimizing matrix — UHTC or other high-temperature fibers not available
  - Presently includes investigation of UHTC fiber composites — currently NASA has SBIRs with companies to develop UHTC fibers
- Computational effort — modeling to better optimize microstructure / properties



# Ultra High Temperature Continuous Fiber Composites



- Image at top right shows dense UHTC matrix with indications of high aspect ratio SiC.
- Image at bottom right shows the presence of C fibers after processing.



# Modeling of UHTCs Will Enhance Development

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## Goals

- Reduce materials development time
- Optimize material properties/tailor materials
- Guide processing of materials
- Develop design approaches

## Approach

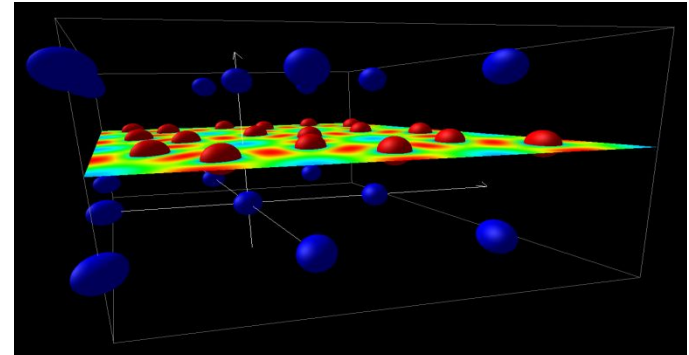
- Develop models integrated across various length scales
- Correlate models with experiment whenever possible



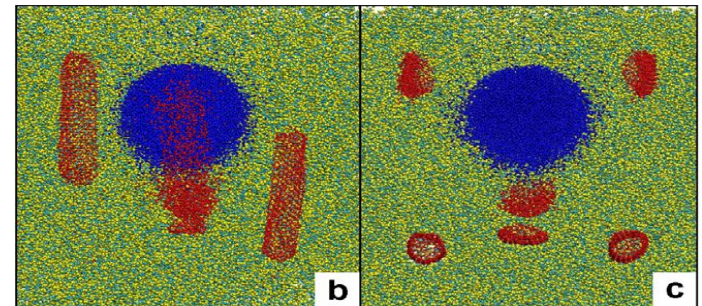


# Multiscale Modeling of Materials

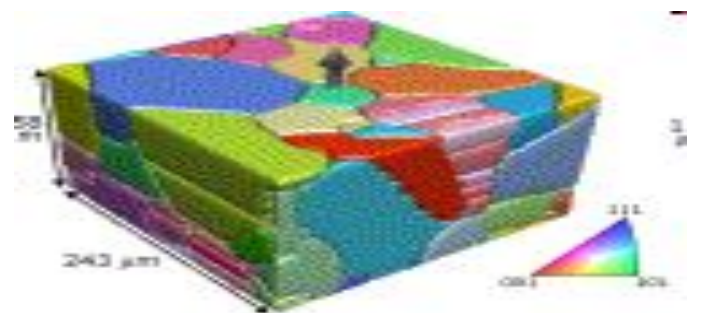
- **Ab initio calculations** — intrinsic material properties
  - *Enables*: structure, bonding, optical and vibrational spectra, chemical reactions, etc
  - *Challenges*: computationally very demanding (very small systems only —  $10^2$  atoms)
- **Atomistic simulations** — localized interfaces, defects, transport, and so forth
  - *Enables*: thermal transport, mechanical properties, interface (for example, grain boundary) adhesion, impurities effects
  - *Challenges*: requires difficult interatomic potential development (except for C, Si, and so forth) (small systems and short time scales —  $10^8$  atoms and  $10^{-9}$  sec)
- **Image-based FEM** — microstructural modeling
  - *Enables*: thermal, mechanical, fracture analysis based on microstructure
  - *Challenges*: requires large database of materials parameters (from experiment or modeling). Nonlinear problems (fracture, plasticity) are very challenging. Macroscopic limit may be difficult.



Lawson, publication in preparation (2010)



Makeev, Sundaresh, and Srivastava, J. Appl. Phys. 106, 014311 (2009)



Lewis and Geltmacher, Scripta Materialia 55 (2006)



# Modeling UHTCs – What's Next?

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- **Accomplishments**

- *Ab initio* calculations of lattice structure, bonding characteristics, elastic constants, phonon spectra and thermal properties of  $\text{ZrB}_2$  and  $\text{HfB}_2$
- *Ab initio* calculations of formation and migration energies for simple defects (vacancies)
- Development of interatomic potentials for  $\text{ZrB}_2$  and  $\text{HfB}_2$  for atomistic simulations

- **Opportunities**

- *Ab initio* calculations of simple/ideal grain boundary structures with and without chemical impurities
- *No UHTC atomistic simulations exist in the literature. New potentials mean the field is wide open!*
- FEM modeling of microstructure to relate processing and properties



# Summary

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- Have investigated number of methods to control microstructure. We have routes to form:
  - *in situ* “composites”
  - Very fine microstructures
- Arcjet testing and other characterization of monolithic materials
- Control oxidation through microstructure and composition
- Beginning to incorporate these materials as matrices for composites
- Modeling effort to facilitate material design and characterization